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⑲ Applicant: Director-General of the Agency of Industrial
Science and Technology
Ministry of International Trade & Industry 3-1
Kasumigasaki 1-chome
Chiyoda-ku Tokyo 100 (JP)

⑳ Inventor: Mizuta, Susumu
858-1, Azuma 3-chome
Tsukuba-shi Ibaraki-ken (JP)

Kumagai, Toshiya
307-301, Matsuhito 3-chome
Tsukuba-shi Ibaraki-ken (JP)

Kondo, Waidchi
823-10, Azuma 2-chome
Tsukuba-shi Ibaraki-ken (JP)

Kawaguchi, Kenji
412-404, Matsushiro 4-chome
Tsukuba-shi Ibaraki-ken (JP)

Shin, Shigemitsu
823-2, Azuma 3-chome
Tsukuba-shi Ibaraki-ken (JP)

Yokota, Hiroshi
Rm. 202, Miyaguchi Mansion 21-3, Nimomiya 3-chome
Tsukuba-shi Ibaraki-ken (JP)

㉑ Representative: Allain, Peter Clerk et al
LLOYD WISE, TREGEAR & CO. Norman House 105-108
Strand
London WC2R 0AE (GB)

㉒ Superconductive material and method of preparing same.

㉓ A superconductive material including a substrate and a superconductive layer of a double oxide of metals provided on the substrate is produced by a method which comprises the steps of:

(a) providing a solution containing a blend of metal compounds having a composition corresponding to that of the double oxide;

(b) applying the solution on the substrate to form a liquid film;

(c) drying the liquid film; and

(d) calcining the dried film to convert the metal compounds into the superconductive double oxide of the metals.

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Description

SUPERCONDUCTIVE MATERIAL AND METHOD OF PREPARING SAME

This invention relates to a superconductive material and to a method of preparing same.

There are now increasing reports on a variety of double metal oxides exhibiting superconductivity. Examples of such oxides include $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_4$, $(\text{La}_{0.9}\text{Ba}_{0.1})_2\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$. These superconductive metal oxides of a ceramic type have thus far been prepared by a vapor phase method or a tape cast method. The former method requires the use of a large, elaborate apparatus. Further, the vapor phase method cannot prepare a superconductive material having a large surface area. The latter method fails to give films with a thin, uniform thickness of less than 20 μm (micrometer). Additionally, the tape cast method requires a high sintering temperature. From the stand point of actual industrial applications, it is highly desirable to provide superconductive materials having various shapes such as thin films, thin wires, tubes and rods. With the known methods, however, it is impossible or extremely difficult to produce ceramic type superconductive materials with such shapes.

With the foregoing problems in view the present invention provides a method of preparing a superconductive material having a superconductive layer of a double oxide of metals provided on a substrate, said method comprising the steps of:

- (a) providing a solution containing a blend of metal compounds having a composition corresponding to that of the double oxide;
- (b) applying said solution on the substrate to form a liquid film;
- (c) drying said liquid film; and
- (d) calcining said dried film to convert said metal compounds to the double oxide of said metals.

In another aspect, the present invention provides a superconductive composite material produced by the above method.

The objects, features and advantages of the present invention will become apparent from the detailed description of the present invention to follow.

The present invention provides a superconductive material including a substrate and a superconductive layer of double oxide of metals provided at least a portion of the surface of the substrate. The superconductive material is produced by a method including the following steps.

(a) Preparation of Coating Solution:

In this step a coating solution containing a blend of metal compounds is prepared. The contents of the metal compounds in the blend are so determined as to provide the desired double oxide of the metals. That is, the molar ratios of the metal compounds in the blend are equivalent to those of the metals in the double oxide. For example, if a superconductive metal oxide having a formula $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_4$ is intended, a coating solution containing La, Sr and Cu compounds and having contents of the La and Sr compounds of 1.8 and 0.2 moles, respectively, per mole of the Cu compound is used.

Any metal compound may be used as long as it gives an oxide upon calcination. A metal compound which is decomposed at a temperature of preferably 1000 °C or below, more preferably 200-900 °C is suitably used. Examples of metal compounds include metal salts of organic or inorganic acids such as naphthenic acid, 2-ethyl hexanoic acid, caprylic acid, stearic acid, lauric acid, butyric acid, propionic acid, oxalic acid, citric acid, lactic acid, phenol, catechol, benzoic acid, salicylic acid, ethylenediaminetetracetic acid, nitric acid, carbonic acid, and hydrochloric acid; metal alkoxides such as ethoxides, propoxides, isopropoxides, butoxides, ethylene glycolides and glycerides; and chelate compounds such as metal acetylacetonates.

Above all, metal compounds having an oxygen atom directly bonded to the metal, such as organic acid salts, alkoxides, acetylacetonates and nitrates, are preferably used because of ease in converting them into metal oxides upon calcination. Organic or inorganic metal compounds used as starting metal compounds and containing no oxygen directly bonded to the metals may be converted into such preferred metal compounds when used in conjunction with a suitable solvent such as an organic acid, an alcohol, acetylacetone or nitric acid.

Any solvent may be used as long as it can dissolve the metal compounds. Examples of suitable solvents include hydrocarbons such as hexane, octane, benzene, toluene and tetralin; alcohols such as methanol, ethanol, propanol, butanol and amyl alcohol; ketones such as acetone, methyl ethyl ketone and acetylacetone; ethers such as dibutyl ether; aldehydes such as acetaldehyde and benzaldehyde; organic acids such as formic acid, acetic acid, propionic acid, butyric acid, caprylic acid, lauric acid, stearic acid, naphthenic acid, linoleic acid, oleic acid, oxalic acid, citric acid, lactic acid, phenol and p-toluic acid; esters such as butylbutylate; amines such as dimethylamine and aniline; amides such as N-methylacetamide and formamide; sulfur compounds such as dimethylsulfoxide; and heterocyclic compounds such as pyridine and furfural. Aqueous solvents such as water, aqueous ammonia and aqueous nitric acid may also be used. These solvents may be used singly or in combination of two or more and suitably selected according to the metal compounds to be dissolved.

The coating solution may be prepared by, for example, dissolving a blend of metal compounds in a solvent. Alternatively, each metal compound is first dissolved in a suitable solvent and, then, the resultant solutions are mixed in suitable proportions. The concentration of the coating solution is not specifically limited but is,

generally, 3-40 % by weight. The coating solution may further contain suitable additives such as a viscosity controlling agent, e.g. polyvinyl alcohol.

(b) Liquid Film Forming Step:

The coating solution obtained in the above step (a) is applied on at least a portion of the surface of a substrate to form a liquid film over that surface. The substrate may be formed of a metal or a metal alloy such as copper, titanium, lead or a stainless steel, a metal oxide such as alumina, zirconia or titania, or a ceramic material such as silicon carbide or graphite. The shape of the substrate is not specifically limited. Substrates having curved or flat surfaces, such as plates, wires, coils, fibers, fabrics, tubes, blocks and rods may be used. Porous substrate may also be used. Coating of the coating solution may be performed by any suitably way such as by a dip coating, spray coating or brush coating method.

(c) Drying of Liquid Film:

The substrate having a coated liquid film is then dried at room or an elevated temperature under ambient or a reduced pressure. It is not necessary to completely dry the film since the drying step is followed by a calcination step at an early stage of which drying may be completed.

(d) Calcination Step:

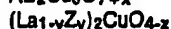
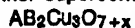
The dried (or semidried) film containing the metal compounds and formed on the substrate is subjected to calcination to convert the metal compounds into the desired superconductive double oxide of the metals.

The calcination temperature varies with the kind of the double oxide, but generally in the range of 500-1000 °C. When the metal compounds are organic compounds, they are decomposed or oxidized at temperatures of 200-500 °C and crystallization or double metal oxide forming reaction takes place at temperatures of 500-1000 °C. Inorganic metal compounds such as metal nitrates, hydroxides, carbonates or halides are decomposed and oxidized to form double metal oxides at temperatures of 1000 °C or below.

The calcination is preferably performed for 0.5 hour or more, more preferably 1-72 hours. The calcination step and the above-described drying step may be conducted separately or continuously. The atmosphere in which the calcination is performed may be, for example, air, oxygen, nitrogen or argon. Calcination in an oxygen-free atmosphere should be followed by calcination in oxygen-containing atmosphere at 500-1000 °C in the calcination step, pressurized condition, ambient pressure or reduced pressure may be used.

The calcination product is then allowed to be cooled to room temperature to obtain a superconductive composite material having a superconductive layer of the double oxide of metals provided over the surface of the substrate. The method of the present invention can form superconductive composite materials having a superconductive layer with a thickness of 0.01-20 μm, especially 0.1-10 μm. The thickness of the superconductive layer may be controlled by adjusting the concentration of the metal compounds in the coating solution or by repeating the coating and calcination steps suitable times.

The method of the present invention is particularly suited for the production of superconductive materials having a superconductive layer of the following oxides. However, the present invention is applicable to any other superconductive metal oxides.



In the above formulae:

A : Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Lu, or a mixture of two or more thereof;

B : Ba, Sr, Ca or a mixture of two or more thereof;

x : a number greater than -1 but less than +1;

Z : Ba, Sr, Ca or a mixture of two or more thereof,

y : a number greater than 0 but not greater than 0.2; and

z : a number less than 1 but not less than 0.

The following examples will further illustrate the present invention.

Example 1

Metal compounds: (Molar ratio of metal)

lanthanum naphthenate (La 1.85)

strontium naphthenate (Sr 0.15)

copper naphthenate (Cu 1.00)

Solvent:

butanol

Concentration of metal compounds:

10 % by weight

Substrate:

alumina thin plate

Calcination:

Atmosphere: air

Temperature: 800 °C

Time: 0.5 hour

Number of repetition:

10 times

Critical temperature:

On set: 30 K

5 Perfect superconductive: 10 K

The metal compounds shown above were mixed with each other and the mixture dissolved in the above solvent to give a coating solution having the total metal compounds concentration shown above and having the molar ratio of the metals as shown above. The coating solution was applied on the substrate shown above by immersing the substrate in the coating solution and the coat was dried in the air. Then the substrate having the dried coat was calcined under the conditions shown above. The immersing, drying and calcining steps were repeated 10 times to give a superconductive material whose electrical resistivity was abruptly decreased at the temperature (on set) shown above and which exhibited perfect superconductivity at the temperature shown above.

15 The above procedure was repeated in the same manner as described using an alumina bar (diameter 1 mm) in place of the alumina plate as a substrate. The resultant superconductive composite materials showed similar critical temperature.

The electrical conductivity was measured by the four terminal method in which four spaced apart electrodes with about 2 mm distance were provided on the superconductive layer by coating a silver paste thereon.

20 Examples 2-23 were conducted to prepare various superconductive materials under conditions as summarized below. In each of Examples 2-23, the procedure including coating, drying and 1st stage calcination steps was repeated in the number indicated below. Thereafter, the 2nd stage calcination was performed in an oxygen-containing atmosphere. The calcined product was then gradually cooled to room temperature.

25 Example 2

Metal compounds: (Molar ratio of metal)

lanthanum caprylate (La 1.90)

barium butyrate (Ba 0.05)

strontium naphthenate (Sr 0.05) copper propionate (Cu 1.00)

30 Solvent:

benzene/acetone/propionic acid (1:1:1)

Concentration of metal compounds:

15 % by weight

Substrate:

35 zirconia thin plate stabilized with yttrium

Calcination:

40		1st Stage	2nd Stage
	Atmosphere:	air	oxygen
	Temperature:	800 °C	800 °C
45	Time:	2 hours	5 hours

Number of repetition:

10 times

Critical temperature:

50 On set: 27 K

Perfect superconductive: 10 K

Example 3

Metal compounds: (Molar ratio of metal)

55 lanthanum butoxide (La 1.90)

barium ethoxide (Ba 0.10)

copper methoxide (Cu 1.00)

Solvent:

propionic acid/ethanol (2:1)

60 Concentration of metal compounds:

20 % by weight

Substrate:

alumina thin plate

65

Calcination:

	1st Stage	2nd Stage	
Atmosphere:	argon	air oxygen	5
Temperature:	500 °C	900 °C 800 °C	
Time:	0.5 hour	1 hour 4 hours	10
Number of repetition:			
10 times			
Critical temperature:			
On set: 30K			15
Perfect superconductive: 8 K			
Example 4			
Metal compounds: (molar ratio of metal)			
lanthanum acetylacetonate (La 1.85)			20
strontium naphthenate (Sr 0.15)			
copper ethoxide (Cu 1.00)			
Solvent:			
pyridine/propionic acid (2:1)			25
Concentration of metal compounds:			
10 % by weight			
Substrate:			
SIC fiber			30

Calcination:

	1st Stage	2nd Stage	
Atmosphere:	argon	oxygen	35
Temperature:	800 °C	600 °C	
Time:	2 hours	2 hours	
Number of repetition:			40
10 times			
Critical temperature:			
On set: 28 K			45
Perfect superconductive: 18 K			
Example 5			
Metal compounds: (molar ratio of metal)			
lanthanum ethoxide (La 1.90)			50
barium butoxide (Ba 0.03)			
strontium caprylate (Sr 0.07)			
copper butyrate (Cu 1.00)			
Solvent:			
acetone/propionic acid (1:1)			55
Concentration of metal compounds:			
10 % by weight			
Substrate: silver thin wire (diameter 100 um)			60

Calcination:

	1st Stage	2nd Stage
5 Atmosphere:	reduced pressure	oxygen
Temperature:	800 °C	570 °C
10 Time:	2 hours	2 hours

Number of repetition:

10 times

Critical temperature:

15 On set: 27 K

Perfect superconductive: 16 K

Example 6

Metal compounds: (Molar ratio of metal)

20 lanthanum isopropoxide (La 1.90)

barium isopropoxide (Ba 0.10)

copper methoxide (Cu 1.00)

Solvent:

propionic acid/ethanol (2:1)

25 Concentration of metal compounds:

15 % by weight

Substrate:

stainless steel thin plate

30 Calcination:

	1st Stage	2nd Stage
Atmosphere:	nitrogen	oxygen
35 Temperature:	850 °C	600 °C
Time:	2 hours	5 hours

40 Number of repetition:

10 times

Critical temperature:

On set: 30 K

45 Perfect superconductive: 23 K

Example 7

Metal compounds: (Molar ratio of metal)

50 yttrium butyrate (Y 1.00)

barium butyrate (Ba 2.00)

copper butyrate (Cu 3.00)

Solvent:

propionic acid/ethanol/acetone (1:1:1)

Concentration of metal compounds:

10 % by weight

55 Substrate:

alumina tube

60

65

Calcination:

	1st Stage	2nd Stage
Atmosphere:	air	oxygen
Temperature:	500 °C	800 °C
Time:	1 hour	2 hours

5

10

Number of repetition:

15 times

Critical temperature:

On set: 95 K

Perfect superconductive: 18 K

15

Example 8

Metal compounds: (Molar ratio of metal)

lanthanum nitrate (La 1.90)

calcium nitrate (Ca 0.10)

copper nitrate (Cu 1.00)

20

Solvent:

acetylacetone/methanol (1:9)

Concentration of metal compounds:

20 % by weight

25

Substrate:

SiC fiber

30

Calcination:

	1st Stage	2nd Stage
Atmosphere:	reduced pressure	oxygen
Temperature:	900 °C	570 °C
Time:	5 min.	2 hours

35

Number of repetition:

8 times

Critical temperature:

On set: 32 K

Perfect superconductive: 15 K

40

45

Example 9

Metal compounds: (Molar ratio of metal)

yttrium acetylacetonate (Y 1.00)

barium acetylacetonate (Ba 2.00)

copper acetylacetonate (Cu 3.00)

50

Solvent:

pyridine/propionic acid (2:1)

Concentration of metal compounds:

10 % by weight

55

Substrate:

zirconia thin plate stabilized with yttrium

60

65

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Calcination:

		1st Stage	2nd Stage
5	Atmosphere:	argon	oxygen
	Temperature:	800 °C	800 °C
10	Time:	1 hour	2 hours

Number of repetition:

10 times

Critical temperature:

15 On set: 90 K

Perfect superconductive: 20 K

Example 10

Metal compounds: (Molar ratio of metal)

20 lanthanum ethoxide (La 1.85)

barium butyrate (Ba 0.15)

copper methoxide (Cu 1.00)

Solvent:

naphthenic acid/butanol/propionic acid (1:1:1)

25 Concentration of metal compounds:

20 % by weight

Substrate:

silver-coated titanium wire (diameter 1 mm)

30

Calcination:

		1st Stage	2nd Stage
35	Atmosphere:	air	oxygen
	Temperature:	800 °C	600 °C
	Time:	1 hour	2 hours

40 Number of repetition:

10 times

Critical temperature:

On set: 13 K

45 Perfect superconductive: 13 K

Example 11

Metal compounds: (Molar ratio of metal)

yttrium stearate (Y 1.00)

60 barium naphthenate (Ba 2.00)

copper naphthenate (Cu 3.00)

solvent:

propionic acid/butanol (1:1)

Concentration of metal compounds:

20 % by weight

55 Substrate:

zirconia thin plate stabilized with yttrium

60

65

Calcination:

	1st Stage	2nd Stage	
Atmosphere:	argon	oxygen	5
Temperature:	500 °C	800 °C	
Time:	0.5 hour	2 hours	10

Number of repetition:

10 times

Critical temperature:

On set: 90 K

Perfect superconductive: 23 K

15

Example 12

Metal compounds: (Molar ratio of metal)

yttrium carbonate (Y 1.00)

barium peroxide (Ba 2.00)

copper oxide (Cu 3.00)

20

Solvent:

nitric acid/acetone (9:1)

Concentration of metal compounds:

5 % by weight

25

Substrate:

alumina porous thin plate

Calcination:

	1st Stage	2nd Stage	
Atmosphere:	air	oxygen	35
Temperature:	900 °C	700 °C	
Time:	5 min.	2 hours	

Number of repetition:

10 times

Critical temperature:

On set: 95 K

Perfect superconductive: 20 K

40

45

Example 13

Metal compounds: (Molar ratio of metal)

yttrium naphthenate (Y 1.00)

barium naphthenate (Ba 2.00)

copper naphthenate (Cu 3.00)

50

Solvent:

toluene or butanol

Concentration of metal compounds:

20 % by weight

55

Substrate:

silver thin plate

60

65

Calcination:

		1st Stage	2nd Stage
5	Atmosphere:	air	oxygen
	Temperature:	500 °C	800 °C
10	Time:	0.5 hour	24 hours

Number of repetition:

10 times

Critical temperature:

15 On set: 80 K

Perfect superconductive: 20-45 K

Example 14

Metal compounds: (Molar ratio of metal)

20 yttrium caprylate (Y 1.00)

barium caprylate (Ba 2.00)

copper caprylate (Cu 3.00)

Solvent:

propionic acid/butanol (1:1)

25 Concentration of metal compounds:

20 % by weight

Substrate:

silver wire

30

Calcination:

		1st Stage	2nd Stage
35	Atmosphere:	argon	oxygen
	Temperature:	500 °C	800 °C
	Time:	0.5 hour	24 hours

40 Number of repetition:

10 times

Critical temperature:

On set: 80 K

45 Perfect superconductive: 25 K

Example 15

Metal compounds: (Molar ratio of metal)

50 yttrium laurate (Y 1.00)

barium laurate (Ba 2.00)

copper laurate (Cu 3.00)

Solvent:

propionic acid/toluene (1:1)

Concentration of metal compounds:

20 % by weight

55 Substrate:

silver-coated copper wire

60

65

Calcination:

	1st Stage	2nd Stage	
Atmosphere:	air	oxygen	5
Temperature:	700 °C	800 °C	
Time:	0.5 hour	24 hours	10
Number of repetition:			
10 times			
Critical temperature:			
On set: 85 K			15
Perfect superconductive: 20 K			
Example 16			
Metal compounds: (Molar ratio of metal)			
yttrium stearate (Y 1.00)			20
barium stearate (Ba 2.00)			
copper stearate (Cu 3.00)			
Solvent:			
propionic acid/toluene (1:1)			
Concentration of metal compounds:			25
20 % by weight			
Substrate:			
platinum thin plate			

Calcination:

	1st Stage	2nd Stage	
Atmosphere:	air	oxygen	30
Temperature:	700 °C	800 °C	35
Time:	0.5 hour	24 hours	
Number of repetition:			40
10 times			
Critical temperature:			
On set: 80 K			45
Perfect superconductive: 20 K			
Example 17			
Metal compounds: (Molar ratio of metal)			
holmium naphthenate (Ho 1.00)			
barium naphthenate (Ba 2.00)			50
copper naphthenate (Cu 3.00)			
Solvent:			
butanol or toluene			
Concentration of metal compounds:			
20 % by weight			55
Substrate:			
zirconia thin plate stabilized with yttrium			

Calcination:

		1st Stage	2nd Stage
5	Atmosphere:	air	oxygen
	Temperature:	700 °C	800 °C
	Time:	0.5 hour	24 hours

10

Number of repetition:

10 times

Critical temperature:

15

On set: 75 K

Perfect superconductive: 30 K

Example 18

Metal compounds: (Molar ratio of metal)

20

heavy rare earth naphthenates (heavy rare earth* 1.00)

barium naphthenate (Ba 2.00)

copper naphthenate (Cu 3.00) (Heavy rare earth : 44 % Er, 40 % Yb, balance Lu and Ho)

Solvent:

butanol or toluene

25

Concentration of metal compounds:

20 % by weight

Substrate:

zirconia thin plate stabilized with yttrium

30

Calcination:

		1st Stage	2nd Stage
	Atmosphere:	air	oxygen
35	Temperature:	700 °C	800 °C
	Time:	0.5 hour	24 hours

40

Number of repetition:

10 times

Critical temperature:

On set: 80 K

Perfect superconductive: 30 K

45

Example 19

Metal compounds: (Molar ratio of metal)

yttrium nitrate (Y 1.00)

barium nitrate (Ba 2.00)

50

copper nitrate (Cu 3.00)

Solvent:

dimethylsulfoxide

Concentration of metal compounds:

20 % by weight

55

Substrate:

zirconia thin plate stabilized with yttrium

60

65

Calcination:

	1st Stage	2nd Stage	
Atmosphere:	air	oxygen	5
Temperature:	900 °C	800 °C	
Time:	5 min.	24 hours	10
Number of repetition:			
10 times			
Critical temperature:			
On set: 80 K			15
Perfect superconductive: 30 K			
Example 20			
Metal compounds: (Molar ratio of metal)			
yttrium nitrate (Y 1.00)			20
barium nitrate (Ba 2.00)			
copper nitrate (Cu 3.00)			
Solvent:			
formamide			
Concentration of metal compounds:			25
20 % by weight			
Substrate:			
strontium titante thin plate			

Calcination:

	1st Stage	2nd Stage	
Atmosphere:	air	oxygen	35
Temperature:	900 °C	800 °C	
Time:	5 min.	24 hours	40
Number of repetition:			
10 times			
Critical temperature:			
On set: 70 K			45
Perfect superconductive: 30 K			
Example 21			
Metal compounds: (Molar ratio of metal)			
yttrium nitrate (Y 1.00)			50
barium nitrate (Ba 2.00)			
copper nitrate (Cu 3.00)			
Solvent:			
N-methylacetamide			
Concentration of metal compounds:			55
10 % by weight			
Substrate:			
barium titante thin plate			

Calcination:

		1st Stage	2nd Stage
5	Atmosphere:	air	oxygen
	Temperature:	900 °C	800 °C
10	Time:	5 min.	24 hours

Number of repetition:
20 times

Critical temperature:
15 On set: 80 K
Perfect superconductive: 35 K

Example 22

Metal compounds: (Molar ratio of metal)
20 yttrium nitrate (Y 1.00)
barium nitrate (Ba 2.00)
copper nitrate (Cu 3.00)

Solvent:

pyridine/propionic acid (2:1)
25 Concentration of metal compounds:
10 % by weight

Substrate:
strontium titanate thin plate

30 Calcination:

		1st Stage	2nd Stage
35	Atmosphere:	air	oxygen
	Temperature:	900 °C	800 °C
	Time:	5 min.	24 hours

40 Number of repetition:
20 times

Critical temperature:
On set: 80 K
45 Perfect superconductive: 30 K

Example 23

Metal compounds: (Molar ratio of metal)
yttrium acetylacetonate (Y 1.00)
50 barium acetylacetonate (Ba 3.00¹)
copper acetylacetonate (Cu 4.30²)

Solvent:

pyridine/propionic acid (5:3)
Concentration of metal compounds:
9 % by weight

55 Substrate:
zirconia thin plate stabilized with yttrium

60

¹ (*: Since barium and copper are also reacted with the yttrium contained in the substrate, the amount of the barium acetylacetonate and copper acetylacetonate are increased. The final superconductive layer has a composition YBa₂Cu₃O₇.)

65 ² (*: Since barium and copper are also reacted with the yttrium contained in the substrate, the amount of the barium acetylacetonate and copper acetylacetonate are increased. The final superconductive layer has a composition YBa₂Cu₃O₇.)

Calcination:

	1st Stage	2nd Stage
Atmosphere:	air	oxygen
Temperature:	500 °C	950 °C
Time:	10 min.	20 min.

Number of repetition:

20 times

Critical temperature:

On set: 97 K

Perfect superconductive: 89 K

15

Claims

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1. A method of preparing a superconductive material having a superconductive layer of a double oxide of metals provided on a substrate, said method comprising the steps of:

(a) providing a solution containing a blend of metal compounds having a composition corresponding to that of the double oxide;

25

(b) applying said solution on the substrate to form a liquid film;

(c) drying said liquid film; and

(d) calcining said dried film to convert said metal compounds into the superconductive double oxide of said metals.

2. A method as claimed in claim 1, wherein said substrate is in the form of a wire or a plate.

30

3. A method as claimed in claim 1, wherein said metal compounds are compounds capable of forming oxides upon calcination at 1000 °C or less.

4. A method as claimed in claim 3, wherein said metal compounds are alkoxides, salts, chelates, halides, hydroxides, peroxides or oxides of said metals.

5. A method as claimed in claim 3, wherein said metal compounds are naphthenates, octylates, caprylates, stearates, laurates, butyrates, propionates, oxalates, citrates, lactates, phenoxides, catechoxides, benzoates, salicylates, ethylenediaminetetracetates, nitrates, carbonates, hydrochlorides, ethoxides, propoxides, isopropoxides, butoxides, ethylene glycoxides, glycerides, acetylacetonates of said metals.

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6. A method as claimed in claim 1, wherein step (d) is performed at a temperature of 500-1000 °C for a period of time of 0.5 hour or more.

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7. A method as claimed in claim 1, wherein steps (a) through (d) are repeated until said superconductive layer has a thickness of 0.01-20 μm.

8. A method as claimed in claim 1, wherein step (d) is performed at a temperature of 500-1000 °C in an oxygen-containing atmosphere.

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9. A method as claimed in claim 8, wherein the calcination in the oxygen-containing atmosphere is preceded by calcination in an oxygen-free atmosphere.

10. A method as claimed in claim 1, wherein said solution contains a first compound selected from the group consisting of Y compounds, La compounds, Nd compounds, Sm compounds, Eu compounds, Gd compounds, Dy compounds, Ho compounds, Er compounds, Yb compounds, Lu compounds and mixtures thereof, a second compound selected from the group consisting of Ba compounds, Sr compounds, Ca compounds and mixtures thereof and a Cu compound so that said double oxide has a formula:

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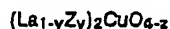


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wherein A stands for Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Lu, or a mixture of two or more thereof, B stands for Ba, Sr, Ca or a mixture of two or more thereof, and x stands for a number greater than -1 but less than +1.

11. A method as claimed in claim 1, wherein said solution contains a La compound, a compound selected from the group consisting of Ba compounds, Sr compounds, Ca compounds and mixtures thereof and a Cu compound so that said double oxide has a formula:

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0 277 020

wherein Z stands for Ba, Sr, Ca or a mixture of two or more thereof, y is greater than 0 but not greater than 0.2 and z is a number less than 1 but not less than 0.

12. A method as claimed in claim 1, wherein said substrate is formed of a metal, metal oxide or a ceramic.

13. A superconductive material obtained by the method according to claim 1.

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